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THE CRYSTAL STRUCTURE OF SATURATED BISLACTAM

GÜLTEN GÜNEL

Faculty of Science and Arts University of Çukurova Adana, Turkey

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ABSTRACT

The crystal structure of saturated bislactam has been determined from three dimensional single crystal X-ray data. The crystals are monolinic, with unit-cell dimensions a= 43.431(2), b= 7.707(1), c= 13.586(1) Å, B= 96.35(1)°, space group C2/c and Z= 8. The structure was solved by direct methods and refined by full-matrix least squares to R= 0.061 for the 3374 independent diffractometer measured reflections. The title compound forms a 1:1 inclusion compound with o-xylne and the molecules have almost perfect C2-symmetry which is a non-crystallographic symmetry.

INTRODUCTION

As a continuation of investigations on the conformational behaviour of medium-ring systems (Ollis et., 1974); (Ollis et al., 1975); (Edge et al., 1981), the X-ray structure analysis of the saturated bislactam was undertaken. The compound is one of a series of medium ring compounds which are conformationally mobile in solution. In addition to the conformational properties several of this series of molecules form inclusion compounds by trapping solvent molecules either in cavities or channels formed by the molecules. In some cases they therefore become potential resolvers of mixed isomers and, exceptionally, when the structure is non-centrosymmetric, can resolve optical enantiomers.

In addition to the information on the solid state conformation of the saturated bislactam, this structure analysis has shown its ability to form an inclusion compound with the solvent. A preliminary account of this work has been published as a short communication. This paper includes the whole reviewed and completed results of X-ray crystal structure of saturated bislactum. The chemical formula of the compound- ignoring the included molecule- is $C_{24}H_{22}N_2O_2$ and the chemical name is -5,18 dimethyl 5, 18- dihydrotribenzo {b, t, j} {1, 4} diaza, cyclododecane -6, 17- dione.

EXPERIMENTAL

The crystals of saturated bislactam were provided by Dr. J.F. Stoddart of the University of Sheffield and re-crystallised by Dr. D.J. Williams from xylene.

Oscillation and Weissenberg photographs showed the crystal to be monoclinic with systematic absences hkl, h+k = 2N+1 and h01, L=2N+1, consistent with space groups Cc and C2/c. From the cell contents and intensity statistics space group was found to be C2/c.

Accurate unit-cell dimensions were obtained by measurement of 20 high-angle α reflections on a diffractometer, and performong a least-squares calculation.

Crystal Data: $C_{24}H_{22}N_2O_2$, M=370, Monoclinic, a=43.431(2), b=7.707(1), c=13.586(1) Å, β=96.35°, U=4520 Å^3, D_c=1.40 gr cm^{-3}, Z=8, Space group C2/c, Cu-K_α radiation, λ=1.5418 Å.

Intensity data were collected for a crystal of dimensions ca. 0.3×0.2×0.4 mm^3 mounted about its b-axis on a Siemens off-line automatic four-circle diffractometer. A five-value measuring procedure (one side of peak, back-ground, full peak, background on other side of peak, other side of peak) was employed (Allen et. al., 1971). Cu-K_α radiation at a take-off angle of 4.5°, a nickel β filter, and a Na(Tl)I scintillation counter were used. A total of 3374 independent reflections (to θ=60°) were measured by use of the θ–2θ scan technique, and 576 of these were judged to be 'unobserved' since their net count was less than 2.58σ. The net count of the 12 0 8 reflection, measured as a reference every 50 reflections, did not alter significantly during the data collection (ca. 6 days) indicating that no deterioration of the crystal had occured. The data were brought to a uniform arbitrary scale by use of this reflection (Allen et al., 1971) and Lotrentz and polarization corrections were applied. (McIntyre and Stansfield, 1988). No absorption corrections were applied.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods. The details of theory as well as the techniques used in crystal structure analysis by direct methods are well documented in authorative texts such as (Woolfson, 1963) and numerous reviews and articles (Hauptman and Karle, 1959); (Karle and Karle 1966); (Hauptman, 1986); (Woolfson, 1988); (Giacovazzo et al., 1988); (Debaerdemaeker, 1988). The structure of the com-

pound was solved by application of the program MULTAN (Main, 1978) to 250 reflections with normalized structure factors (E's)>1.50. An E map calculated for the phase solution with the highest 'combined figure of merit' gave plausible positions for all the non-hydrogen atoms of the structure. These atoms were refined anisotropically by full-matrix least squares to give a residual R=0.085. A difference map contained sharp peaks corresponding to all the hydrogen atoms. These were for subsequent refinements fixed at calculated positions 1.0 Å from their parent carbon atoms. Nine reflections which had $|F_o| \ll |F_c|$ were suspected of being affected by extinction and therefore removed. Further refinement, the hydrogens isotropically, the remaining non-hydrogen atoms anisotropically, reduced R to a final value of 0.061. The maximum residual electron density in the final difference map was 0.3 e $Å^{-3}$ Unit weights were used throughout the refinements. Atomic scattering factors were taken from (Doyle-Turner, 1968) with the exception of those for hydrogen which were taken from (Stewart et al., 1965). The computations were carried out on the Imperial College CDC 6400, the University of London CDC 6600 and 7600, and the University of Çukurova IBM 4361 computers using, in the main, programs belonging to the X-ray 72 System (Stewart et al., 1972).

RESULTS AND DISCUSSION

The final fractional atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms together with their estimated standard deviations, are listed in Tables 1 and 2. High values of the estimated standard deviations of the fractional atomic coordinates for the atoms C(19(, C(20), C(21), C(22) and C(23) are consistent with the high values of the anisotropic thermal parameters of these atoms. These are the atoms of the guest molecules in the structure. Hence this structure analysis has shown that saturated bislactam forms a 1:1 inclusion compound with o-xylene. The guest molecules are disordered and assume two distinct orientations in the inclusion regions of the host lattice.

The structure of the guest molecule together with the thermal-vibration ellipsoids is shown in Figure 1 (Johnson, 1965).

The fractional atomic coordinates for the hydrogen atoms are given in Table 3.

The bond lengths and angles together with their estimated standard deviations are listed in Tables 4 and 5. Most of the bond lengths and

Table 1. Fractional coordinates for the non-hydrogen atoms with estimated standart deviations in parentheses

Atom	x	y	z
C(1)	.8272(1)	.0261(4)	.5101(2)
C(2)	.8424(1)	−.0901(4)	.4547(3)
C(3)	.8727(1)	−.0597(5)	.4387(2)
C(4)	.8880(1)	.0855(5)	.4793(2)
C(4A)	.8731(1)	.2023(4)	.5356(2)
N(5)	.8894(1)	.3539(3)	.5751(2)
Me(5)	.8999(1)	.4746(5)	.5022(2)
O(6)	.8914(1)	.2482(3)	.7305(1)
C(6)	.8975(1)	.3646(4)	.6744(2)
C(6A)	.9146(1)	.5236(5)	.7146(2)
C(7)	.9451(1)	.4996(5)	.7564(3)
C(8)	.9622(1)	.6380(7)	.7975(3)
C(9)	.9493(1)	.8012(6)	.7974(3)
C(10)	.9188(1)	.8255(5)	.7578(3)
C(10A)	.9009(1)	.6874(4)	.7170(2)
C(11)	.8672(1)	.7167(4)	.6812(2)
C(12)	.8454(1)	.6340(5)	.7498(2)
C(12A)	.8116(1)	.6543(4)	.7101(2)
C(13)	.7930(1)	.7700(5)	.7554(3)
C(14)	.7622(1)	.7975(5)	.7187(3)
C(15)	.7497(1)	.7098(5)	.6359(3)
C(16)	.7676(1)	.5947(5)	.5891(2)
C(16A)	.7985(1)	.5659(4)	.6528(2)
O(17)	.8221(1)	.4873(3)	.4827(2)
C(17)	.8165(1)	.4463(4)	.5663(2)
N(18)	.8259(1)	.2913(3)	.6071(2)
Me(18)	.8154(1)	.2207(5)	.6983(3)
C(18A)	.8423(1)	.1739(A)	.5499(2)
C(19)	−.0110(?)	.0100(20)	.0223(7)
C(20)	−.0293(3)	.1328(20)	.0283(6)
C(21)	−.4757(3)	.2504(16)	.0198(8)
C(22)	.0226(3)	.0862(19)	−.0761(10)
C(23)	−.5106(3)	.2796(16)	.0888(7)

angles are around the normal values, however few of them deviate from the expected values. The bond lengths C(4A)-N(5) and C(18A)-N(18) are slightly longer than the corresponding C-N bond length in a peptide linkage in which the nitrogen atom bonds to an sp^3 hybridized carbon. The bond lengths C(6)–N(5) and C(17)-N(18) are slightly shorter than the corresponding C-N bond length in a peptide linkage in which the nitorgen atom bonds to an sp^2 hybridized carbonyl carbon. Here, it is clear that there is considerable delocalization of π electrons in C(6)-N(5) and C(17)-N(18) and these bonds have partial double bond character. On the other hand the bonds C(4A)-N(5) and C(18A)-N(18) are almost single bond type despite the sp^2 hybridized forms of C(4A) and C(18A). This is because there are no effective overlap of p-orbitals of carbon and

Table 2. Anisotropic thermal parameters* ($\times 10^3 Å^2$) for the non-hydrogen atoms with standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	52(2)	40(2)	42(2)	−5(2)	−2(2)	3(2)
C(2)	74(3)	37(2)	36(2)	−3(2)	−2(2)	−2(2)
C(3)	76(3)	40(3)	35(2)	8(2)	9(2)	−4(2)
C(4)	55(2)	35(2)	37(2)	6(2)	12(2)	−1(2)
C(4A)	47(2)	36(2)	29(2)	1(1)	4RJ)	1(1)
N(5)	43(1)	38(2)	31(1)	−4(1)	8(1)	−2(1)
Me(5)	65(2)	51(2)	41(2)	−17(2)	16(2)	−0(2)
O(6)	71(2)	49(2)	40(1)	−1(1)	1(1)	10(1)
C(6)	38(2)	44(2)	36(2)	7(2)	(4)1	0(1)
C(6A)	36(2)	52(2)	31(2)	−1(2)	3(1)	−4(2)
C(7)	40(2)	73(3)	47(2)	8(2)	0(2)	−6(2)
C(8)	34(2)	104(4)	55(2)	−6(2)	−2(2)	−16(2)
C(9)	47(2)	85(2)	51(2)	−21(2)	5(2)	−20(2)
C(10)	49(2)	54(2)	44(2)	−9(2)	8(2)	-8(2)
C(10A)	36(2)	47(2)	31(2)	−4(2)	3(1)	-2(1)
C(11)	39(2)	42(2)	41(2)	−1(2)	0(1)	0(1)
C(12)	38(2)	53(2)	33(2)	1(2)	?(1)	−3(2)
C(12A)	36(2)	42(2)	37(2)	−0(2)	6(1)	3(1)
C(13)	47(2)	51(2)	48(2)	−3(2)	12(2)	−9(2)
C(14)	45(2)	54(2)	65(2)	6(2)	19(2)	−3(2)
C(15)	35(2)	60(2)	63(2)	6(2)	7(2)	4(2)
C(16)	40(2)	52(2)	46(2)	−0(2)	1(1)	2(2)
C(16A)	37(2)	36(2)	36(2)	1(1)	6(1)	4(1)
O(17)	63(1)	47(1)	43(1)	6(1)	8(1)	5(1)
C(17)	35(2)	38(2)	35(2)	−3(1)	−1(1)	−0(1)
N(18)	43(1)	36(1)	34(1)	1(1)	10(1)	3(1)
Me(18)	64(2)	51(2)	47(2)	3(2)	21(2)	12(2)
C(18A)	45(2)	35(2)	30(2)	2(1)	3(1)	3(1)
C(19)	34(4)	144(9)	52(5)	-35(5)	11(3)	-50(6)
C(20)	189(10)	257(16)	80(5)	−136(11)	−18(6)	-2(7)
C(21)	218(12)	172(10)	151(9)	38(9)	−28(5)	−24(8)
C(22)	159(9)	206(13)	210(12)	71(9)	−104(9)	−107(11)
C(23)	191(10)	196(11)	127(7)	−68(8)	−7(7)	41(8)

* In the form: $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

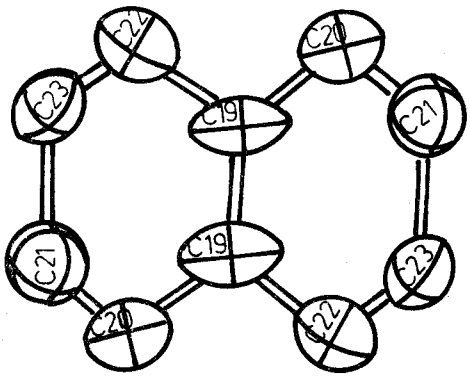

FIGURE 1. Structure of the guest molecule together with the thermal-vibration ellipsoids

Table 3. Fractional coordinates of the hydrogen atoms*

Atom*	x	y	z
H(11)	.8050	.0046	.5215
H(21)	.8314	-1983	.4258
H(31)	.8839	-.1438	.3973
H(41)	.9107	-1071	.4685
H(51)	.8914	.4417	.4330
H(52)	.8935	.5967	.5155
H(53)	.9235	.472ɔ	.5058
H(71)	.9548	.3788	.7573
H(81)	.9843	.6188	.828ɔ
H(91)	.9622	.9038	.8260
H(101)	.9092	.9467	.7587
H(111)	.8629	.8454	.5758
H(112)	.8626	.6658	.6123
H(121)	.8505	.5063	.7578
H(122)	.8492	.6896	.8175
H(131)	.8024	.8358	.8165
H(141)	.7491	.8817	.7535
H(151)	.7274	.7300	.6085
H(161)	.7585	.5308	.5273
H(181)	.8255	.1050	.7145
H(182)	.8215	.3021	.7555
H(183)	.7925	.2063	.6908

* The numbering of the hydrogen atoms is that of the atoms to which they are bonded.

Table 4. Bond lengths (Å) with standard deviations in parentheses

Bond		Length	Bond		Length
C(1)	C(2)	1.382(5)	C(12)	C(12A)	1.513(4)
C(2)	C(3)	1.378(6)	C(12A)	C(13)	1.393(5)
C(3)	C(4)	1.385(5)	C(13)	C(14)	1.388(5)
C(4)	C(4A)	1.387(5)	C(14)	C(15)	1.373(5)
C(4A)	C(18A)	1.391(4)	C(15)	C(16)	1.381(5)
C(1)	C(18A)	1.393(4)	C(16)	C(16A)	1.394(4)
C(4A)	N(5)	1.439(4)	C(16A)	C(12A)	1.398(4)
N(5)	Me(5)	1.469(4)	C(16A)	C(17)	1.503(4)
N(5)	C(6)	1.358(4)	C(17)	O(17)	1.229(4)
C(6)	O(6)	1.226(4)	C(17)	N(18)	1.361(4)
C(6)	C(6A)	1.501(5)	N(18)	Me(18)	1.471(5)
C(6A)	C(7)	1.395(4)	N(18)	C(18A)	1.433(4)
C(7)	C(8)	1.382(6)	C(18A)	C(1)	1.393(5)
C(8)	C(9)	1.377(7)	C(19)	C(20)	2.245(20)
C(9)	C(10)	1.388(5)	C(20)	C(21)	1.148(19)
C(10)	C(10A)	1.396(5)	C(21)	C(23)	1.716(20)
C(10A)	C(6A)	1.398(5)	C(23)	C(22)	1.162(19)
C(10A)	C(11)	1.507(4)	C(22)	C(19)	1.192(19)
C(11)	C(12)	1.539(5)			

Table 5. Bond angles (°) with standard deviations in parentheses

Bonds			Angle	Bonds			Angle
C(4A)	N(5)	C(6)	118.8(3)	C(18A)	C(4A)	N(5)	121.2(3)
N(5)	C(6)	C(6A)	118.2(3)	N(18)	C(18A)	C(1)	119.2(3)
N(5)	C(6)	O(6)	121.6(3)	C(18A)	C(1)	C(2)	120.6(3)
Me(5)	N(5)	C(6)	124.5(3)	N(5)	C(4A)	C(4)	119.5(3)
N(5)	C(6)	C(6A)	118.2(3)	C(4A)	C(4)	C(3)	120.7(3)
C(6)	C(6A)	2C(10A)	123.3(3)	C(11)	C(10A)	C(10)	119.5(3)
C(6A)	C(10A)	C(10)	118.5(3)	C(10A)	C(10)	C(9)	121.2(4)
C(6)	C(6A)	C(7)	116.7(3)	C(12)	C(12A)	C(13)	119.8(3)
C(6A)	C(7)	C(8)	120.4(4)	C(12A)	C(13)	C(14)	121.5(3)
C(6A)	C(10A)	C(11)	121.9(3)	C(17)	C(16A)	C(16)	116.2(3)
C(10A)	C(11)	C(12)	112.5(3)	C(16A)	C(16)	C(15)	120.4(3)
C(11)	C(12)	C(12A)	112.2(3)	C(17)	N(18)	Me(18)	124.3(3)
C(12)	C(12A)	C(16A)	122.2(3)	O(17)	C(17)	N(18)	121.4(3)
C(12A)	C(16A)	C(17)	123.4(3)	C(19)	C(20)	C(21)	113.2(13)
C(16A)	C(17)	N(18)	118.0(3)	C(20)	C(21)	C(23)	127.4(15)
C(17)	N(18)	C(18A)	118.5(3)	C(21)	C(23)	C(22)	128.3(14)
N(18)	C(18A)	C(4A)	121.3(3)	C(23)	C(22)	C(19)	115.6(14)

nitrogen atoms due to the torsional stresses imposed on them by the benzene rings and the carbonyl groups.

However, in neither case the degree of bond modification is as large as that normally associated with delocalization effects in amides (Marsh, R.E., 1968).

Figure 2 shows a stereo view of the molecule (Johnson, 1965) with the numbering scheme used and the torsion angles around the central 12-membered ring. The angles between the aromatic planes A and B; A and C; and B and C are 36°, 39° and 38° respectively.

The principal torsion angles about the C-N bond in amide groups (178° and 180°) are almost equal.

The trans amides linking rings A and B, and A and C are inclined to the mean planes of their adjacent rings with approximately same angles, and have their N-methyl groups on opposite sides of the 12-membered ring. The trans olefinic linkage between rings B and C is inclined to the rings B and C with equal angles of 70°. It may be summarized that the equivalent torsional angles are all very nearly equal and are distributed within the 12-membered ring such that the molecule has almost perfect C2 symmetry. The non-crystallographic two fold axis of symmetry is bisecting the mid-points of the C(2)-C(3); C(4a)-C(18a), and C(11) C(12) bonds. The symmetry of the molecule is shown more clearly in Figure 3.

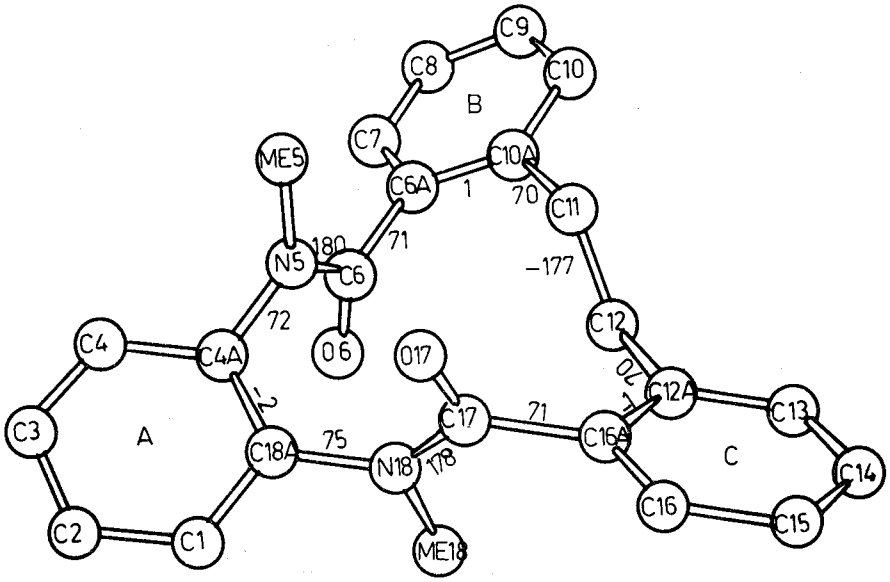

FIGURE 2. The solid state conformation of the saturated bislactam showing the torsional angles

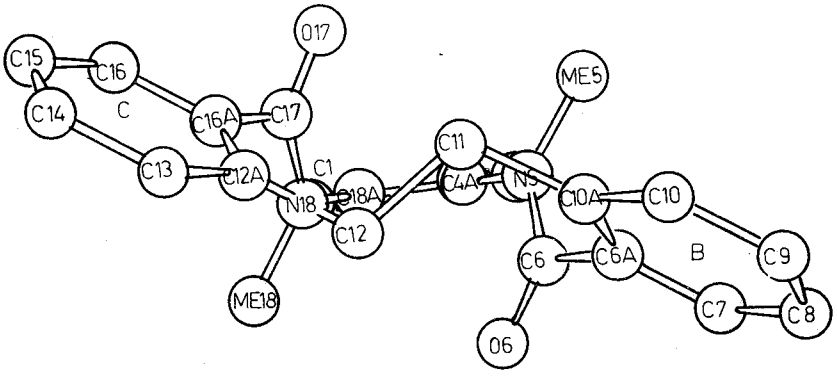

FIGURE 3. The solid state conformation of the saturated bislactam showing its C2-symmetry

Figure 4 shows a stereo view of the packing of the molecules in the structure (Johnson, 1965).

Some selected intra- and intermolecular contacts ($\leq$3,5 Å) are given in Table 6. In accordance with these values the structure is fairly loosely

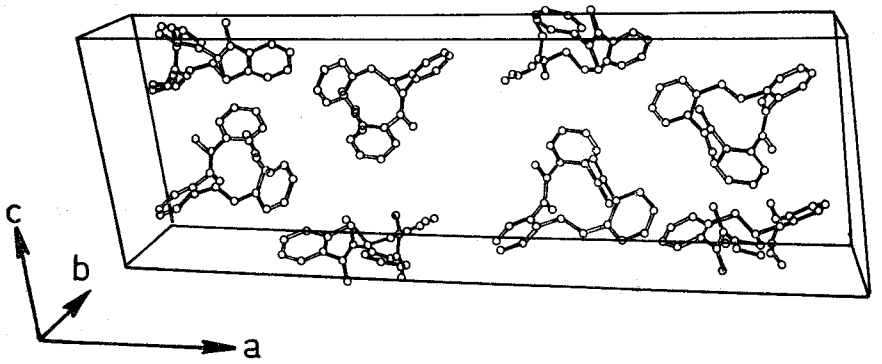

FIGURE 4. A stereoscoipc view of the packing of the molecnles

packed. This is consistent with the fact that in the saturated molecular-crystals, the molecules are bonded with weak bonds known as van der Waals forces (Pauling, 1960).

Table 6. Selected intra-and intermolecular contacts $\leq$ 3,5 Å *

Atoms		Distance (A)	Atoms		Distance (A)
C(11)	N(5)	3.34	C(17)	N(5)	3.24
O(17)	N(5)	3.22	N(18)	C(6)	3.19
N(18)	O(6)	3.15	C(6)	C(11)	3.12
C(17)	C(11)	3.30	C(17)	C(A4)	3.16
C*(3)	O(6)	3.36	C*(15)	C(16)	3.41
C*(4)	C(10)	3.49	C*(2)	O(17)	3.40)

* Symmetry operated atoms are indicated by an asterisk.

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REFERENCES

ALLEN, F.H., ROGERS, D., and TROUGHTON, P.G.H. 1971, Acta Cryst. B 27, 1325.

DEBAERDEMAEKER, T., 1988, Acta Cryst., A 44, 353–357.

DOYLE, P.A., TURNER, P.S., 1968, Acta Cryst., A 24, 390.

EDGE, S.J.: OLLIS, W.D.: STEPHANATOU, J.S.; STODDART, F.; WILLIAMS, D.J. and MENA A.W., 1981, Tetraedron Letters, 22, No. 23, 2229–2232

GIACOVAZZO, C., CASCARANO, G., and CHAO-DE, Z., 1988, Acta Cryst. A 44 45—51.

HAUPTMAN, H., 1986, Science (USA) 233, no. 4760, 178–182

HAUPTMAN, H., KARLE, J. 1959 Acta Cryst. 12, 93.

JOHNSON, C.K., 1965, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, I. and KARLE, I.L., 1966 Acta, Cryst. 21, 849.

MAIN, P., 1978, MULTAN 78, Department of Physics University of York-England.

MARSH, R.E.; DONOHUE, J., 1968, Advanc. Protein Chem., 23, 288

McINTYRE, G.J. and STANSFIELD, R.F.D., 1988, Acta Cryst. A 44, 257.

OLLIS, W.D.;, STODDART, J.F., and NOGRADI, M., M., 1975, Angew. Chem. Internat. Edn. 14, 168.

OLLIS, W.D.; STODDART, J.F., and SUTHERLAND, I.O., 1974, Tetrahedron, 30, 1903 and refs. therein.

PAULING, L., 1960, "The Nature of the Chemical Bond" Cornell University Press, Ithaca, 3rd. Ed. 246.

STEWART, J.M., KUNDELL, F.A., BALDWIN, J.C.: 1972 X-Ray System of Crystallographic Programs, University of Maryland Technical Report TR 646, revised version.

STEWART, R.F.; DAVIDSON, R.E., SIMPSON, W.T.; 1965 J. Chem Phys., 42 3175.

WOOLFSON, M.M. 1963 Direct Methods in Crystallography, Oxford University Press, New York.

WOOLFSON, M.M., 1988, Acta Cryst., A 44, 222–225.